Comparison of the Efficiency of Ultraviolet/Ultrasonic (UV/US) and Ultraviolet/Zinc Oxide (UV/ZnO) Technologies as Advanced Oxidation Processes in the Removal of Linear Alkylbenzene Sulfonate (LAS), an Anionic Detergent, from Aqueous Media

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ABSTRACT

Surfactants are one of the most commonly found xenobiotics in municipal and industrial wastewater. The purpose of this study was to compare ultraviolet/ultrasonic (UV/US) and ultraviolet/zinc oxide (UV/ZnO) processes in the removal of LAS from aqueous media.In this study, a medium-pressure UV lamp (125 W), an ultrasonic device (400 W and 42 kHz), and ZnO nanoparticles (NPs) were used. The concentration of LAS was 0.5, 14, and 21 mg/L in all experiments. Contact time of 8, 16, and 24 minutes, pH of 3, 7, and 11, and NP concentrations of 50, 100, 150 mg/L were selected. Detergent extraction was performed using methylene blue active substances.The results showed that the efficiency of UV/US process in the removal of LAS was 89.35%, while the removal efficiency of UV/ZnO process was 81.27%. In both processes, the rate of detergent removal increased by elongating the contact time from 8 to 24 minutes. The efficiency of UV/US process in LAS removal was greater than that of the UV/ZnO process. The findings showed that the removal efficiency of UV/US process was directly correlated with pH, while it had an inverse correlation with the removal efficiency of UV/ZnO process.

Keywords: Linear alkylbenzene sulfonate, Ultraviolet light, Acoustic waves, Zinc oxide nanoparticles.

INTRODUCTION

Surfactants are one of the most commonly found xenobiotic in municipal and industrial wastewater, which can lead to environmental pollution by entering the environment [1].Surfactants are generally divided into four non-ionic, anionic, cationic, and amphoteric groups[2, 3]. Ionic surfactants constitute two-thirds of all surfactants and account for more than 90% of ionic surfactants [4]. Among anionic surfactants, anionic linear alkylbenzene sulfonate (LAS) detergents are the most extensively used household detergents, with applications in washing powder, dishwashing liquid, and other household cleaners [5]. LAS can cause toxicity in aquatic organisms at low concentrations of approximately 1 mg/L. Considering its resistance to biodegradation, LAS by accumulating in the body of aquatic organisms affects the natural water balance and threatens the health of aquatic organisms, animals, and humans [6-8]. Moreover, if LAS enters water sources, it can produce negative ions and cause aquatic plants

to grow rapidly in aquatic environments, leading to eutrophication. Consequently, decomposition of aquatic plants reduces the amount of dissolved oxygen for aquatic life and causes sewage oxidation [9]. The average concentration of surfactants in domestic wastewater is 1-10 mg/L and may reach as high as 21 mg/L [10, 11]. LAS concentrations in domestic wastewater range from 3 to 21 mg/L [12]. It is known that anionic detergents have low purity due to their resistance to biological treatment. These resistant compounds, when entering the host environment or areas such as wastewater treatment plants, show slower decomposition or absorption, compared to normal compounds [13]. Therefore, they cannot be completely eliminated by conventional treatment methods and cause environmental problems by entering the host water [14].

Conventional methods reported so far for the removal of surfactants from water include chemical deposition, adsorption, membrane technology, and various biological methods, which are time-consuming and expensive [15]. In recent decades, advanced oxidation technologies have been recognized as the most efficient option for degradation of toxic substances, particularly in wastewater treatment plants, which have properties such as chemical stability and low biodegradability [16]. In advanced oxidation processes, removal of pollutants is based on the production of highly oxidizing free hydroxyl radicals that convert many organic compounds to minerals [17]. These free radicals, which are highly oxidizing, attack organic matter molecules, remove a hydrogen atom from the organic material, and improve degradation [18].

Ultraviolet (UV) radiation is one of the methods used in recent years for water and wastewater treatment. UV radiation lies along the electromagnetic spectrum in the 100-400 nm range and is divided into three categories: type A (315-400 nm), type B (280-315 nm), and type C (200-280 nm). UV disinfection of water usually occurs in the range of 200-280 nm (type C). When water or effluent is exposed to UV light, hydroxyl radicals are produced as strong oxidizers and readily oxidize organic compounds[19]. Ultrasonic (US) method is another important method for this purpose. In this method, the audio frequency is higher than 16 kHz, which exceeds the human hearing range (16-10,000 Hz). The mechanism of action of US in decomposition of organic compounds involves hydroxyl radical formation, thermal decomposition, and hydro mechanical shear force [20].

Ultrasonic waves in the aqueous solvent lead to the formation and destruction of gas bubbles (cavitation) and induce high transient pressure and temperature, resulting in free radical formation in water (OH and OOH). These radicals penetrate into water and oxidize organic compounds. It is known that hydrogen peroxide is formed by free radicals (OH and OOH)[21]. Common advantages of UV/US method include: 1) non-production of mutagenic or carcinogenic byproducts; 2) low space requirements for installation of UV and US systems; 3) lack of smell or taste disorders; and 4) lack of need for using or storing dangerous chemical compounds [22]. The mechanism of action in the combined UV/US system involves hydrogen peroxide formation by US waves from water molecules, followed by conversion to hydroxyl radicals by UV irradiation [23].

The photocatalytic method using nanoparticles (NPs) is one of the advanced oxidation processes, which has been increasingly used in recent years, with applications in water and wastewater treatment. In the last two decades, photocatalysis by semiconducting materials, such as zinc oxide (ZnO), has attracted much attention given its high optical sensitivity, high stability, non-toxic nature, wide energy gap, and high efficiency in electron formation. Considering the energy gap property, much of the UV spectrum is absorbed by these NPs [24]. The catalyst cost and toxicity are some of the limitations of water treatment. ZnO NPs are

desirable in this respect and are being developed for widespread use [25]. Generally, the mechanism of action involves UV radiation of the semiconductor material and excitation of electrons from the valence band to the conduction band, resulting in the production of hydroxyl radicals [23]. The ZnO/UV process is one of the most important photocatalytic processes under development [26]. ZnO with a 3.2 kV band gap and wavelength of 387 nm can be excited under irradiation in the UVA range of 320-380 nm [27]. When ZnO NPs are exposed to UV radiation in the visible range, electrons are excited and activated from the valence band to the conduction band, creating a hole in the valence band that is highly active. They may be absorbed directly by the organic contaminant and react with the catalyst surface or indirectly through hydroxyl radicals. The activated electrons which move to the conduction band also react with organic materials by forming different radicals, such as superoxide and hydroxyl radicals [26]. ZnO has three major advantages: semiconduction with a band gap of 3.37 eV and high exciton binding energy (60 mV); near-UV emission; and safety and biocompatibility[25]. The most important advantage of ZnO is its ability to absorb a wide range of electromagnetic waves, besides its photocatalytic potential in exposure to UVA radiation. In fact, non-toxic ZnO has chemical stability at high temperature and is capable of chemical oxidation [28]. In recent years, application of photocatalytic processes has increased owing to the limitations of common methods for detergent removal from aquatic environments. These limitations include the high cost of chemical processes, possible formation of toxic byproducts during treatment, difficult transfer of a compound from one phase to another in the adsorption process, clogging of membranes and filtration limitations in membrane technology, high sludge production, and gradual process of biological methods [29]. According to the studies conducted so far, no report on LAS removal using two methods simultaneously included UV/US and UV/ZnO processes have been reported.This study aimed to provide two methods for removing pollutants without deteriorating environmental safety of LAS, to determine the association of synergistic effects of UV/US, contact time,pH, and ZnO dose for UV/ZnO processes.Therefore, considering the advantages of combined UV/ZnO process and UV/US radiation in the removal of LAS detergent, in this study, we aimed to compare these two methods and determine their efficiency in LAS removal.

EXPERIMENT
Measurement methods
Methodswas measured using methylene blue active substances (MBAS) according to C5540 method described in the book of Standard Methods for Examination of Water and Wastewater [30].

Experimental procedures
Preparation of stock solution ("mother" solution): Having a LAS solution density of 0.8628 g/cm^3, the required amount of harvesting was equal to 1.2 cc according to the formula $[(\rho = m/v)]$ for preparation of the mother solution. The solution was diluted to volume (1000) in a volumetric flask and refrigerated for one week to prevent decomposition.

Preparation of standard solution
This solution was prepared from the stock solution. To prepare a 100-ppm standard solution with a volume of 200 cc ($v_1c_1 = v_2c_2$), 20 cc of the stock solution was diluted in a 200 mL volumetric flask using distilled water; the standard solution was prepared daily.

Preparation of the required reagents

Methylene blue reagent: For this purpose, 100 mg of methylene blue powder was dissolved in 100 mL of water, and then, 30 mL of the solution was transferred to a 1000 mL volumetric flask. Next, 40 mL of normal sulfuric acid (6.0 N) and 50 g of monobasic phosphate with a $NaH_2PO4.H_2O$ molecule were added and shaken to dissolve; finally, it was diluted to a volume of 1000 mL.Washing solution: In a 1000 mL flask, 500 mL of water, 41 mL of normal sulfuric acid (6.0 N), and 50 g of monobasic sodium phosphate were added and stirred until completely dissolved to reach a final volume of 1 L.

Complex formation and extraction

First, 50 cc of the sample was added to a 500 cc separatory funnel. After adding a drop of phenolphthalein to the funnel, it was moved in circular motions. Then, one drop of NaOH was added until the solution turned pink. After adding a drop of 1 N sulfuric acid, the funnel was stirred until the solution became colorless.Methylene blue reagent (25 cc) was removed to form a methylene blue cation in the medium. Next, 10 mL of chloroform was added, stirred for about 30 seconds (a complex is formed if it is stirred for more than 30 seconds), and kept under static conditions. It should be noted that the aqueous phase was on top of the organic phase (chloroform) because it was heavier.After transferring the organic phase to a 250 cc separatory funnel, 10 mL of chloroform was added to the remaining solution in the 500 cc separatory funnel, shaken for 30 seconds, and held still; the organic phase was transferred to a 250 cc separatory funnel similar to the previous step.After adding 10 mL of chloroform to the remaining solution in the 500 cc separatory funnel, it was shaken for 30 seconds and held still; next, the organic phase was transferred to the 250 cc separatory funnel.A washing solution (50 mL) was added to the 250 cc separatory funnel solution (to purify the complex solution and remove impurities entering the solution), shaken for 30 seconds, and held still. Next, the lower organic phase was transferred to a 25 cc volumetric flask; this process was repeated three times consecutively. Finally, the solution inside the volumetric flask (result of three repetitions) was brought to the desired volume with chloroform.Measurements: Absorbance was determined at a wavelength of 652 nm against chloroform as the control in a spectrophotometer.

UV process

The UV lamp used in this study was a 125 W medium-pressure UV lamp with a wavelength of 254 nm. Because this lamp produces a lot of heat, we used an aluminum foil around buccal surfaces to prevent radiation exposure. Different concentrations of the sample (0.5, 14, and 21 mg/L) in different pH ranges (3, 7, and 11) were exposed to UV light for 8, 16, and 24 minutes. Finally, the detergent was extracted, and absorbance was read by a spectrophotometer.

US process

A 2.5 L ultrasonic device with a frequency of 42 kHz was used in this study. The contact time and pH were the same as the previous stage. The detergent was extracted in the final step, and absorbance was read by a spectrophotometer.

UV/US process

The sample was placed in an ultrasonic device after exposure to UV irradiation within the same contact time as the previous stage. Finally, it was extracted, and absorbance was read.

UV/ZnO process

First, LAS concentrations of 0.5, 14, and 21 mg/L were prepared, and pH was adjusted to 3, 7, and 11, using 1 N hydrochloric acid and 1 N NAOH. Next, 50, 100, and 150 mg/L of ZnO NPs were added. The solution was placed in a shaker for 30 minutes in the dark to achieve adsorption-desorption balance. The sample was then exposed to UV radiation for 8, 16, and 24 minutes and passed through a Büchner funnel, connected to a pump with a 0.45 μm cellulose acetate filter to prevent the effect of NPs on detergent extraction. Finally, the detergent was extracted, and absorbance was read by a spectrophotometer.

Sample size and sampling

The sample size (total number of experiments) in the first step (UV/US method) was measured to be 3×3×3×3=81 according to the pH range, contact time, and different concentrations of LAS in three replicates of the experiment. Since the Taguchi method was used to analyze the data, there was no need to repeat the experiments; only the experiment with optimal factors was repeated three times. In the second step (UV/ZnO method), Taguchi design method was employed. For each concentration of the pollutant in the first, second, and third stages of the study, nine experiments were carried out based on the Taguchi design, and the removal efficiency was measured. The total number of experiments was 54; the optimal experiment was repeated three times. According to the Taguchi method, the factor levels were divided into controllable (signals) and uncontrollable (noise) in each experiment. The signal-to-noise (S/N) ratio was measured to determine the optimal experiment or the optimal combination of different factor levels for an optimal response. Calculation of S/N ratio depends on the type of optimization. In this study, Taguchi experiment design was used to reduce the number of trials and decrease the cost and time required for the research. Since in this study, percentage of detergent removal was evaluated as the response, the goal was to optimize it[31].

RESULT AND DISCUSSION

The results are demonstrated in graphs and tables in this section. Considering the study objectives, the outcomes of two UV/ZnO and UV/US processes in the removal of LAS detergent from synthetic solutions are presented with respect to the effects of contact time, pH, catalyst concentration, and LAS removal in the nanophotocatalyst process.

Results of combined UV/US process

Figures 1 and 2 illustrate the effects of pH and contact time on the sequential sonophotolysis process. Sonodegradation of LAS were applied for 8, 16, and 24 minutes at pH of 3, 7, and 11. Substantial LAS degradation was expected after 24 minutes. Based on the findings, degradation efficiency increased as time advanced. Based on the present results, the removal percentage increased with time. In this process, contact time of 24 minutes was more effective than other contact times, and alkaline pH=11 had greater effects than acidic pH= 3 and neutral pH= 7. The relationship between the pH and the percentage of the detergent removal is significant. In order to ensure the accuracy of the results, all UV, US, and UV/US processes were repeated three times. The mean and standard deviation of repeated experiments are presented in Table 1.

Synergistic effects of UV/US

The synergistic effect of UV/US is attributed to optical degradation, ultrasonic decomposition, and ozone oxidation. UV radiation with wavelengths below 200 nm causes oxygen to produce ozone. Therefore, UV radiation in the upper air levels of the reactor produces ozone, which results in the pollutant decomposition after transfer to the solution. However, transfer of ozone to a liquid solution is directly related to the intermediate phase between liquid and gas. This phase substantially expands due to the boiling of liquid surface as a result of ultrasound wave flow, leading to the transfer of ozone to the solution. High removal efficiency of the hybrid UV/US process is attributed to the sonochemical cavitation, direct photolysis by UV light, and oxidizing activities of ozone and hydroxyl radicals in the process of detergent decomposition. Overall, formation of hydroxyl radicals is associated with ozone photolysis, sonolysis, and thermal decomposition in cavitation bubbles[32]. In a study comparing the efficacy of sonolysis, photolysis, and sonoptolysis processes in organic matter decomposition, Mahlambi et al. concluded that combination of two methods caused a significant increase in phenol breakdown through three major mechanisms, including photochemical decomposition, sonochemical oxidation, and ozone-induced oxidation by UV radiation in the photosonic reactor[33]. In another study by WU on C.I. Reactive Red 198 dye in the sonocatalytic process, the removal efficiency of UV/US process was greater than that of the US process alone due to the production of oxidizing radicals in the environment[34].

Effect of catalyst concentration

Figure 3 illustrates the effect of NP concentration on the removal of LAS detergent in the photocatalytic process. Increase of ZnO dose up to 50 mg/L, improved the removal efficiency, but 150 mg/l of nanoparticles reduced the degradation efficiency,the optimal NP concentration was 100 mg/L. In other words, as the catalyst concentration increases, the number of active sites in the solution increases and reaches a level where light penetration is ineffective owing to the high particle concentration.Due to photocatalytic oxidation reactions at the catalyst surface, as the amount of ZnO increases, the number of active sites and catalyst surface increase, as well; therefore, all detergent molecules are absorbed by the catalyst, resulting in a high rate of detergent degradation[35]. According to a study by Kaur and Singh., on the removal of Reactive Red 198 dye from wastewater using the photocatalytic process, an increase in NP mass improved the removal efficiency as the number of active sites on the catalyst increased, resulting in the enhancement of UV entrapment and contaminant uptake[36]. One study reported similar results in their study, illustrating that the excess dosage of catalys could cause a light-screening effect that decreases the surface area of catalyst being exposed to light irradiation and eventually decreases the photocatalytic efficiency[37].Hoffman et al., reported that the reason of decrease in the efficiency with increasing ZnO nanoparticle concentration was the phenomenon of nanoparticle dispersion and the lack of ZnO chain production on catalyst surface[38].

Effect of pH

According to Figure 4, in an acidic medium (pH= 3), the removal efficiency was higher than that reported in neutral and alkaline media because of the positive charge of the catalyst surface in acidic environments, resulting in the adsorption of anionic detergent with negative charge; therefore, detergent degradation occurred and removal efficiency increased. A previous study showed that electrostatic repulsion occurred between the surface charge of ZnO and the anionic surfactant at high pH (pH= 12). Moreover, the results of a study by Mijin et al., on the

photocatalytic decomposition of metamitron by the UV/ZnO process revealed that the efficiency of photocatalytic degradation was higher at acidic pH, compared to alkaline pH[39].

Effect of contact time

As presented in Figure 5, removal efficiency increases by elongating the contact time because more adsorption occurs between the detergent and NPs, which eventually leads to greater removal. In fact, collision of UV light with the ZnO surface leads to the release of an electron-hole pair. Therefore, more electrons are produced by increasing the radiation time, and the detergent removal efficiency increases[40]. In this regard,Ku and Jung.,in their study on the removal of chromium-6 using the photocatalytic process, concluded that increasing the contact time improves the removal efficiency[41].The optimal UV/ZnO process was repeated three times to ensure the accuracy of the experiments, as shown in Table 2.

Comparison of UV/US and UV/ZnO processes

According to the results, under similar conditions, including contact time and experiment location, the UV/US process showed greater removal efficiency than the UV- and US alone, and UV/ZnO processes, as shown in Figure 6. In this Figure, the UV process is shown with level 1, the US process is shown with level 2, the UV/ZnO process is shown with level 3, and the UV/US process is shown with level 4. The chemical processes of ultrasonic irradiation are found on the phenomenon of acoustic cavitation, cavitation serves as a way of concentrating the diffused energy of ultrasound into US and UV/US reactors with the simultaneous discharge of reactive radicals with each reactor serving as a hot spot. In the absence of UV light, only around 8% of the LAS concentration decreased by physical adsorption and UV photolysis was able to achieve partial degradation of the LAS[42]. The addition of ZnO to the UV-illuminated process led to an enhancement in the removal of all LAS and increased at higher ZnO loading[42].
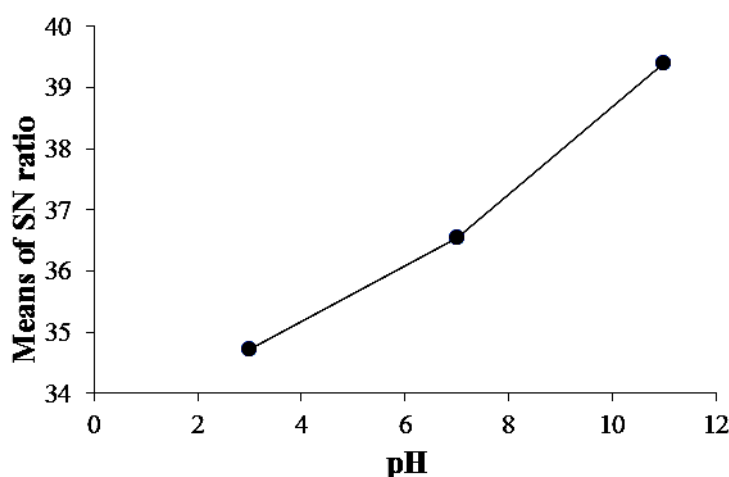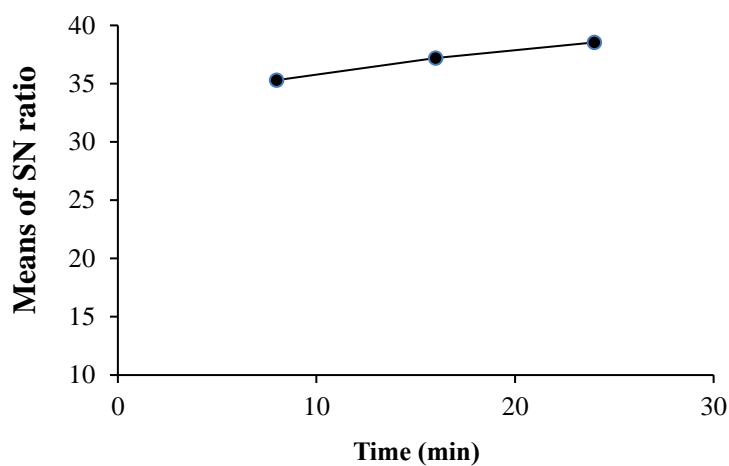

Figure 1. Effect of pH in UV/US reactor
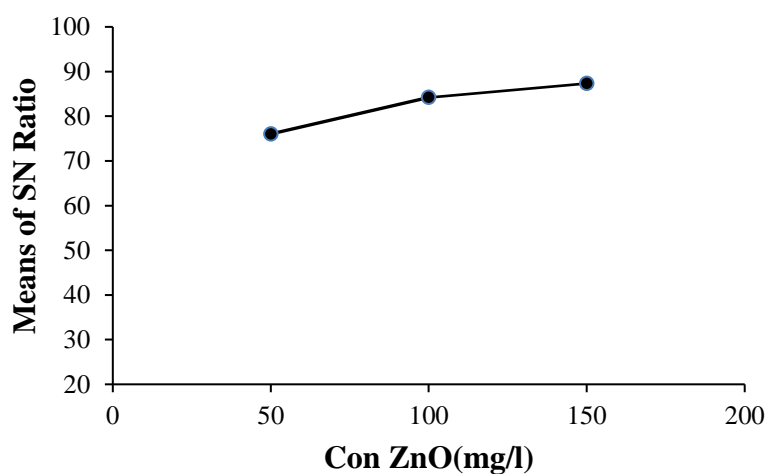
Figure 2. Effect of contact time in US reactor

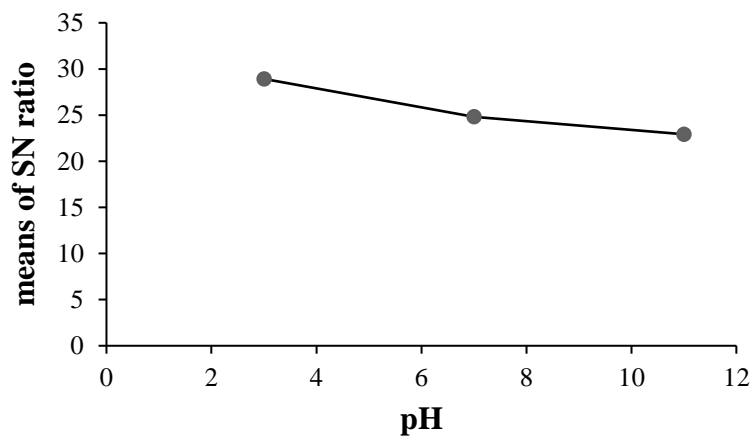**Figure 3.** Effect of concentration of ZnO in VU/ZnO reactor
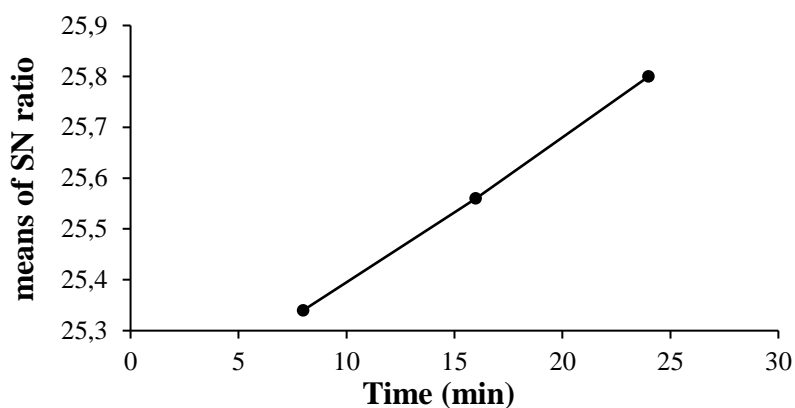

Figure 4. Effect of pH in UV/ZnO reactor

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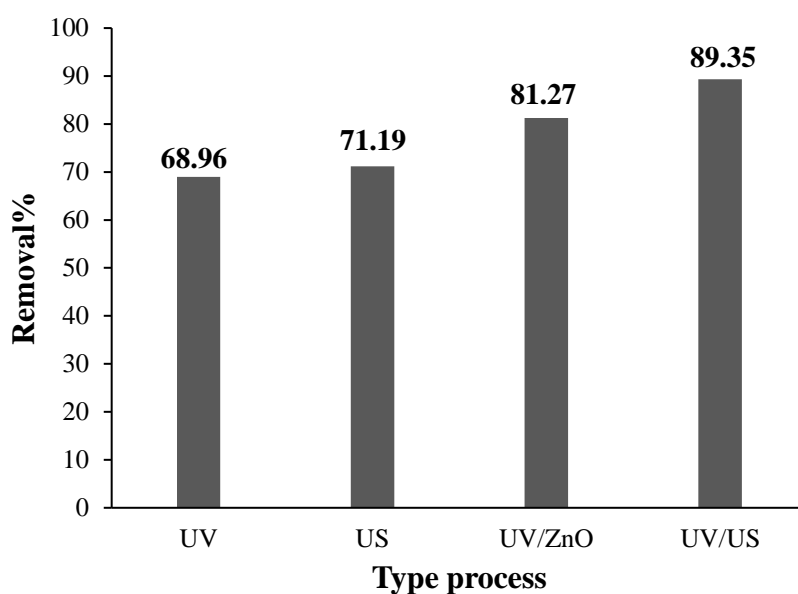**Figure 5.** Effect of contact time in US reactor

Figure 6. The removal efficiency of UV, US,UV/ZnO and UV/US processes

Table 1. Mean±SD of UV,US and UV/ZnO processes

Type process	Concentration(mg/l)		
	0.5	14	21
UV	69.96±0.49	54.31±0.253	35.04±0.107
US	71.19±0.61	65.99±0.036	38.63±0.131
UV/US	89.35±1.218	71.11±0.218	53.81±1.476

Table 2. Mean±SD of UV/ZnO process

Type of process	Concentration(mg/L)		
	0.5	14	21
UV/US	81.27±0.701	54.31±0.253	39.37±0.229

CONCLUSION

The present findings showed that the removal efficiency improved by increasing the contact time in all processes used to remove LAS. In the sequential UV/US process, the rate of detergent degradation was higher at alkaline pH compared to acidic pH, and therefore, the removal efficiency was higher. On the other hand, in the UV/ZnO process, the removal efficiency was higher at acidic pH, compared to alkaline pH. The results showed that the removal efficiency improved by increasing the concentration of ZnO NPs. In all processes evaluated in this study (UV/US and UV/ZnO), a lower pollutant concentration was associated with a higher removal efficiency; this finding is generally attributed to the greater efficacy of the produced hydroxyl radicals. Based on the findings, the removal efficiency of UV/US process was higher than that of the UV/ZnO process and more economically acceptable (because of the high cost of ZnO NPs and filtration). Also, the time required for the nanophotocatalyst process was longer than the time required for photosonolysis since NPs must remain in the dark for 15 minutes, and the sample must pass through a filter prior to extraction by a funnel.

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REFERENCES

[1] Cokgor, E.U., Arslan-Alaton, I., Erdinc, E., Insel, G., and Orhon, D., *Water Sci. Technol*, **2007**, 55(10), 155-163.

[2] Arslan-Alaton, I., Akin, A., and Olmez-Hanci, T., *Photochem Photobiol. Sci*, **2011**, 10(3), 396-402.

[3] Arslan-Alaton, I., Akin, A., and Olmez-Hanci, T., *J. Chem. Technol. Biotechnol*, **2010**, 85(4), 493-501.

[4] Ayranci, E., and Duman, O., *J. Hazard. Mater*, **2007**, 148(1-2), 75-82.

[5] Bindes, M.M., and Franco Jr, M.R., *Desalin. Water. Treat*, **2015**, 56(11), 2890-2895.

[6] Özdemir, O.M., Çınar, M., Sabah, E., Arslan, F., and Celik, M.S., *J. Hazard. Mater*, **2007**, 147(1-2), 625-632.

[7] Lv, W., Bazin, B., Ma, D., Liu, Q., Han, D., and Wu, K., *J. Pet. Sci. Eng*, **2011**, 77(2), 209-218.

[8] Upadhyaya, A., Acosta, E.J., Scamehorn, J.F., and Sabatini, D.A., *J Surfacant Deterg*, **2007**,10(4), 269-277.

[9] Pham, T.D., Tran, T.T., Pham, T.T., Dao, T.H., and Le, T.S., *J. Mol. Liq*, **2019**, 287, 110900.

[10] Zhang, C., Valsaraj, K.T., Constant, W.D., and Roy, D., *Water Res.*, **1999**, 33(1), 115-124.

[11] Ambily, P.S, Rebello, S., Jayachandran, K., and Jisha, M.S, *Water Sci. Technol,* **2017**,76(8), 2167-2176.

[12] Libralato, G., Ghirardini, A.V., and Avezzù, F., *J. Environ. Manage*, **2012**, 94(1), 61-68.

[13] Duman, O., and Ayranci, E., *J. Hazard. Mater*, **2010**, 174(1-3), 359-367.

[14] Zhang, X., Zhang, X., Wang, S., Liu, M., Tao, L., and Wei, Y., *Nanoscale*, **2013**, 5(1), 147-150.

[15] Guo, F., Pilot-scale study of removal of anionic surfactants with trickling filter, University of British Columbia, **2008**.

[16] Priti, V.R., and Hemangi, H.D., *J. Environ. Res. Develop*, **2012**, 7(2A), 851-862.

[17] Adak, A., Bandyopadhyay, M., and Pal, A., *Sep. Purif. Technol*, **2005**, 44(2), 139-144.

[18] Aloui, F., Kchaou, S., and Sayadi, S., *J. Hazard. Mater*, **2009**, 164(1), 353-359.

[19] Oparaku, N.F, Mgbenka, B.O, and Ibeto, C.N., *J. Environ. Sci. Technol*, **2011**, 4(1), 73-78.

[20] Nasseri, S., Vaezi, F., Mahvi, A.H., Nabizadeh, R., and Haddadi, S., *J. Environ. Health Sci. Eng*, **2006**, 3(2), 109-116.

[21] Jyothi, K.P., Yesodharan, S., and Yesodharan, E.P., *Ultrason Sonochem*, **2014**, 21(5), 1787-1796.

[22] de Vidales, M.J.M., Barba, S., Sáez, C., Cañizares, P., and Rodrigo, M.A., *Electrochim. Acta*, **2014**, 140, 20-26.

[23] Oturan, M.A., and Aaron, J.J., *Crit. Rev. Env. Sci. Technol*, **2014**, 44(23), 2577-2641.

[24] Saravanan, R., Sacari, E., Gracia, F., Khan, M.M., Mosquera, E., and Gupta, V.K., *J. Mol. Liq*, **2016**, 221, 1029-1033.

[25] Soltani, R.D.C., Rezaee, A., Khataee, A.R., and Safari, M., *J. Ind Eng Chem*, **2014**, 20(4), 1861-1868.

[26] Elmolla, E.S., and Chaudhuri, M., *Desalination*, **2010**, 252(1-3), 46-52.

[27] Kim, S.J., Kim, S.C., Seo, S.G., Lee, D.J., Lee, H., Park, S.H., and Jung, S.C., *Catal. Today*, **2011**, 164(1), 384-390.

[28] Lee, K.M., and Hamid, S.B.A., *Materials*, **2015**, 8(1), 339-354.

[29] Al-Rasheed, R.A., Water treatment by heterogeneous photocatalysis an overview, 4th *SWCC acquired Experience Symposium* held in Jeddah, **2005**, 1-14.

[30] Eaton, A.D., Clesceri, L.S., Rice, E.W., and Greenberg, A.E.,Standard Methods for the Examination of Water and Wastewater,**2005**, 19th ed, American Public Health Association, Water Environment Federation Washington, DC.1-134

[31] Davis, R., and John, P., *Statistical Approaches with Emphasis on Design of Experiments Applied to Chemical Processes*, **2018**, 137, 137-155.

[32] Huang, X., Leal, M., and Li, Q., *Water Res*, **2008**, 42(4-5), 1142-1150.

[33] Mahlambi, M.M., Ngila, C.J., and Mamba, B.B., *J. Nanomater*, **2015**, 2015, 1-29.

[34] Wu, C., and Linden, K.G., *Water Res*, **2008**, 42(19), 4780-4790.

[35] Daneshvar, N., Aber, S., Dorraji, M.S., Khataee, A.R., and Rasoulifard, M.H., *Sep. purif. Technol*, **2007**, 58(1), 91-98.

[36] Kaur, S., and Singh, V., *J .Hazard. Mater*, **2007**, 141(1), 230-236.

[37] Klavarioti, M., Mantzavinos, D., and Kassinos, D., *Eviron. Int*, **2009**, 35(2), 402–417.

[38] Razavi, T., Fadaei, A., Sadeghi, M., and Sedehi, M., *J. Ecol .Eng,* **2020**, 21(6), 1-7.

]39[Mijin, D., Savić, M., Snežana, P., Smiljanić, A., Glavaški, O., Jovanović, M., and Petrović, S., *Desalination*, **2009**, 249(1), 286-292.

[40] Dehghani, M., and Fadaei, A., *Res. J. Chem. Environ*, **2012**, 16, 1-9.

[41] Ku, Y., and Jung, I.L., *Water Res*, **2001**, 35(1), 135-142.

[42] Shokri, M., Isapour, G., Behnajady, M.A., and Dorosti, S., *Desalin Water Treat,* **2015**, 57(27), 12874-12881.